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Hierarchical $Ni_{0.54}Co_{0.46}O_2$ nanowire and nanosheet arrays grown on carbon fiber cloth for high-performance supercapacitors

Yuanzhi Jiang [a, b], Lijuan Zhang [a, b], Hang Zhang [a, b], Cui Zhang [a, b, *], Shuangxi Liu [a, b, **]

[a] Institute of New Catalytic Materials Science, School of Materials Science and Engineering, Nankai University, Tianjin 300071, PR China
[b] Tianjin Collaborative Innovation Center for Chemistry & Chemical Engineering, Tianjin 300071, PR China

HIGHLIGHTS

- $Ni_{0.54}Co_{0.46}O_2$ grown on carbon fibers as binder-free electrode for supercapacitor directly.
- The coexistence of Ni^{2+} and Ni^{3+} in $Ni_{0.54}Co_{0.46}O_2$ could boost the performance.
- The products exhibit outstanding specific capacity and rate performance.
- Symmetrical device delivers excellent energy density and power density.

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ABSTRACT

Hierarchical $Ni_{0.54}Co_{0.46}O_2$ architectures composed by nanowires or nanosheets were successfully grown on bio-mass carbon fiber cloth (CFC) by hydrothermal method. The morphology of $Ni_{0.54}Co_{0.46}O_2$ can be effectively controlled by using different precipitators. The structural effects of the two kinds of morphologies were researched. the results suggest that the $Ni_{0.54}Co_{0.46}O_2$ nanosheet arrays grown on CFC (NCO-NSs/CFC) shows a higher Faradaic areal capacity of 438 μAh cm^{-2} (238.1 mAh g^{-1}) at a current density of 1 mA cm^{-2} and still about 90.3% initial capacity retention even at the high current density of 50 mA cm^{-2}. Moreover, an all-solid-state flexible symmetric supercapacitor device has been successfully assembled. The optimized device delivers superior electrochemical performance with an outstanding energy density of 92.4 Wh kg^{-1} at a power density of 207.2 W kg^{-1}. Such hierarchical nanostructure composed by well-aligned uniform $Ni_{0.54}Co_{0.46}O_2$ nanosheet arrays grown on bio-mass carbon fiber cloth might hold great promise as battery-type electrode material for high-performance supercapacitor.

1. Introduction

Energy is one of the most important topics that attracting more and more attention of the whole world in the 21st century. To meet the urgent requirements of renewable and sustainable energy sources, there is a growing demand for developing cleaner and more efficient energy storage systems such as supercapacitors and lithium-ion batteries [1]. Supercapacitor is regarded as one of the most promising avenue to the future for its relatively higher power density, faster charge/discharge capability and longer cycling life [1–3].

However, the realization of that strategic conception depends on many aspects particularly a breakthrough in obtaining higher energy meanwhile keeping power delivery and cycling stability [4]. One promising approach is to introduce a battery-type faradaic electrode into hybrid electrochemical capacitors [2]. Transition metal oxides as battery-type materials used in capacitors explored relatively higher performance than EDLCs due to their rich redox reactions on the surfaces as well as in the bulk of the electrode [5–10]. At present, a series of transition metal oxides electrode materials, such as MnO_2 [11,12], NiO [13–15] and Co_3O_4 [16], have been researched. However, the applications of these materials are mainly restricted by various aspects as low energy capacity and poor cycle life [17]. $NiCo_2O_4$ with spinel structure sparked world-wide interest as an attractive battery-type faradaic electrode for

* Corresponding author. Institute of New Catalytic Materials Science, School of Materials Science and Engineering, Nankai University, Tianjin 300071, PR China.
** Corresponding author. Institute of New Catalytic Materials Science, School of Materials Science and Engineering, Nankai University, Tianjin 300071, PR China
E-mail addresses: zhangcui@nankai.edu.cn (C. Zhang), sxliu@nankai.edu.cn (S. Liu).

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advanced capacitor devices for the presence of Ni^{2+}/Ni^{3+} and Co^{2+}/Co^{3+} redox couples in the spinel structure [18–20]. What is remarkable is that the addition of Co can largely reduce the specific capacity though effectively improve the cycling life and the conductivity of the Ni–Co oxides [21]. Significantly, according to some researches, the specific capacity is found to be relied on the molar ratio of Co/Ni, getting highest at Co/Ni molar ratio of close to 1 when forming the NaCl-type $NiCoO_2$ [22,23]. $NiCoO_2$ has also been used in many other fields such as water oxidation [24] as well as Li-ion batteries [25] and both of them exhibit excellent performance confirming $NiCoO_2$ has enormous potential in the application of electrochemical reactions.

In recent researches, there were two main nanostructures have raised a widely attention called nanorods/nanowires and nanosheets synthesized by hydro-/solvo-thermal method [26,27]. There were some reports demonstrated that the electrochemical performances such as ion transfer rates and electrode/electrolyte interface properties are strongly influenced by the morphologies and microstructures of electrode materials [28]. In addition, it is well known that defects in materials can improve the performance of supercapacitors, because crystalline imperfection can provide additionally electrochemical active sites. Thus, it is very significate and prospective to study the difference between the different shapes of $NiCoO_2$ with abundant lattice imperfection and its electrochemical properties, which were few researches on before.

Traditionally, when discrete particles are used as electrode materials for supercapacitors, electrodes have to be fabricated with a lot of insulating polymer binder and conductive agents, which can largely affect the capacity performance, portability, price and practicability of supercapacitors. Carbon fiber supported electroactive nanocomposites seems to be a promising plan, with the unprecedented superiority of excellent flexibility, lightweight as well as corrosion resistance. However, most of the as-prepared carbon fibers used for electrode materials are carbon nanotubes, graphene and commercial carbon fiber [29–31]. Given their complex preparation, cost and abundance, the bio-mass carbon derived from bio-base resources such as hemp [8], flax [11] and cotton [32] has attracted intense interest lately and is widely used in SCs. As far as we know, the previous study of $NiCoO_2$ used as electrodes for supercapacitors had to be blended with binders and affect the performance seriously due to the lower conductivity than $NiCo_2O_4$, so it is urgent need to develop an effective binder-free method to achieve the best performance of $NiCoO_2$ [32].

In this work, we successfully synthesized controllable morphology of hybrid nanostructures composed of $Ni_{0.54}Co_{0.46}O_2$ nanowire and nanosheet arrays grown on bio-mass carbon fiber cloth (CFC) through a facile hydrothermal method. A large number of lattice defects and crystalline imperfection were obtained in both morphologies which could boost the chemical performance of supercapacitors effectively and thus form non-stoichiometry $Ni_{0.54}Co_{0.46}O_2$, denoted as NCO-NWs/CFC and NCO-NSs/CFC, respectively. Urchin-like and flower-like $Ni_{0.54}Co_{0.46}O_2$ were prepared by the same method without supporting on the CFC, denoted as NCO-NWs and NCO-NSs separately. As expected, two different nanostructures loaded on CFC directly as binder-free for SCs exhibit high Faradaic capacity. In comparison, NCO-NSs/CFC as a hybrid battery-type electrode exhibit a higher capacity (438.6 μAh cm^{-2} at a current density of 1 mA cm^{-2}), better rate capability (387.0 μAh cm^{-2} at 50 mA cm^{-2}) and capacity retention (~70% after 10000 cycles at 10 mA cm^{-2}) than NCO-NWs/CFC. Moreover, a symmetric supercapacitor device composed of as-prepared NCO-NSs/CFC electrodes has been successfully assembled. The excellent device delivers an outstanding energy density of 92.4 Wh kg^{-1} at a power density of 207.2 W kg^{-1}.

2. Experimental section

2.1. Materials synthesis

2.1.1. Preparation of carbon fiber cloth (CFC) derived from cotton textile

Cotton textile cloth was purchased from a cloth market and cut into strips with the size of 6 × 40 cm^2 without drying and other treatments before carbonization. The carbonization process was carried out by the temperature control program depicted in Fig. S1.

2.1.2. Synthesis of $Ni_{0.54}Co_{0.46}O_2$ NWs/CFC, $Ni_{0.54}Co_{0.46}O_2$ NSs/CFC, $Ni_{0.54}Co_{0.46}O_2$ NWs and $Ni_{0.54}Co_{0.46}O_2$ NSs

All the reagents used in the experiments were analytical grade and without further purification. In a typical experiment, carbon fiber cloth was cleaned in 5 M HCl aqueous solution, acetone, deionized (DI) water and absolute ethanol under ultrasonic for each 15 min, and then dried in an oven over night. $Ni(NO_3)_2{\cdot}6H_2O$ (3.6 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (3.6 mmol) and urea (35 mmol) were addition into a mixed solvent of DI water (40 mL) and ethanol (20 mL) under stirring to form a clear solution. The solution was then transferred to a Teflon-lined stainless steel autoclave followed by putting a piece of cleaned CFC (4 cm × 4 cm) and kept in a vacuum for 3 h in order to ensure the sufficient infiltrate of the precursor solution. After hydrothermal reaction at 100 °C for 8 h, the carbon fiber cloth covered with NiCo-NWs precursor was carefully taken out and rinsed several times with DI water and absolute ethanol, respectively, and finally dried in vacuum at 80 °C for 12 h. In order to get NCO-NWs/CFC, the samples were then annealed at 300 °C in argon for 3 h with the heating rate of 1 °C min^{-1}. NCO-NSs/CFC could be obtained by the method above, except substituting hexamethylenetetramine (HMT) for the urea. Urchin-like NCO-NWs and flower-like NCO-NSs powder were synthesized as contrast samples through the method above except for the use of carbon fiber cloth.

2.2. Characterization

The morphologies were characterized by field-emission scanning electron microscopy (SEM; JEOL, JSM-7500F) and transmission electron microscopy (TEM; FEI, Tecnai-G2-F20). The specific surface area and pore size distribution performance were measured using a BET analyzer (MICROMERITICS, Tristar-3000/ASAP2000) at 77 K. Crystallographic information was collected by powder X-ray diffraction (XRD; Bruker AXS GmbH, BrukerD8 FOCUS). Thermogravimetric analysis (TGA; NETZSCH, TG-209) was carried out under a flow of air with a temperature ramp of 5 °C min^{-1} from room temperature to 750 °C. The surface chemical compositions were examined by X-ray photoelectron spectroscopy (XPS; Axis Ultra DLD). The composition of element was detected by Inductive Coupled Plasma Emission Spectrometer (ICP; Theremo Elemental, IRIS Intrepid II XSP).

2.3. Electrochemical measurements

Electrochemical properties of the $Ni_{0.54}Co_{0.46}O_2$/CFC electrodes were first evaluated with three electrode system measured in a CHI 660E (Chenhua, Shanghai) electrochemical workstation at room temperature. 2 M KOH solution was used as the supporting electrolyte. As-synthesized NCO-NWs/CFC or NCO-NSs/CFC with the valid size of 1 × 1 cm^2 were used as working electrode, directly. Pt gauze and the Hg/HgO were used as the counter electrode and the reference electrode, respectively. Through the careful measurement, the areal quality of NCO-NWs/CFC and NCO-NSs/CFC are 11.6 and 11.4 mg cm^{-2} and the mass loading are 1.9 mg cm^{-2} and